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Method of preparing zirconia film.

Abstract:

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A zirconia film is prepared by coating a substrate with a zirconium acetylacetonate suspension formed into a sol obtained by carrying out hydrolysis of zirconium acetylacetonate by adding water in an amount of from 10 to 12 mols per mol of zirconium acetylacetonate in an organic solvent solution comprising zirconium acetylacetonate, or an organic solvent solution comprising zirconium acetylacetonate and a different type of acetylacetonate metallic complex added, followed by heating at a temperature not lower than 200 DEG C. Data supplied from the esp@cenet database - Worldwide

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54 Method of preparing zirconia film.

57 A zirconia film is prepared by coating a substrate with a zirconium acetylacetonate suspension formed into a sol obtained by carrying out hydrolysis of zirconium acetylacetonate by adding water in an amount of from 10 to 12 mols per mol of zirconium acetylacetonate in an organic solvent solution comprising zirconium acetylacetonate, or an organic solvent solution comprising zirconium acetylacetonate and a different type of acetylacetonate metallic complex added, followed by heating at a temperature not lower than 200°C.

## Description

## Method of preparing zirconia film

## BACKGROUND OF THE INVENTION

This invention relates to a method of preparing a zirconia film, and more particularly to a method of preparing a zirconia film by using a zirconium acetylacetonate suspension formed into a sol (or colloidal solution).

Known as methods for preparing zirconia films at low temperatures are (1) a method in which a substrate is coated with a zirconium alkoxide solution comprising zirconium propoxide or zirconium butoxide, followed by hydrolysis and dehydration condensation (Japanese Patent Publication No. 48865/1984, (2) a method in which a substrate is coated with a zirconium octylate solution followed by thermal decomposition (Japanese Unexamined Patent Publication No. 41770/1986), and (3) a method in which a substrate is coated with an organic solvent solution comprising zirconium acetylacetonate or an organic solvent solution comprising zirconium acetylacetonate and a different type of acetylacetonate metallic complex added, followed by heating at temperatures of not less than 200°C to form it into a zirconia film (Japanese Unexamined Patent Publication No. 76881/1985).

However, in the method (1), hydrolysis and dehydration condensation reaction of zirconium alkoxide proceed extremely rapidly and moreover the moisture in the air cause the reaction to proceed, so that it is difficult to form films with a uniform coating and reproducibility. In addition, an attempt to increase the concentration of an alcohol solution of the zirconium alkoxide to obtain a thick film by the first coating may result in formation of the surface into a gel because of the hydrolysis caused by the moisture in the air to produce a white zirconium gel layer on the zirconium film. For this reason the zirconium film can not be made uniform, and the white zirconium gel layer must be removed before the film can be made uniform. In order for the zirconium gel layer not to be produced, the concentration of the zirconium alkoxide may be lowered to retard the rate of hydrolysis in the air, but a lowered concentration makes it necessary to carry out the coating several times to obtain a thick film, thus increasing the coating times.

In the method (2), on the other hand, the hydrolysis rate of the zirconium octylate is lower than that of the zirconium alkoxide, and hence no gel is formed even when coated with its alcohol solution having a higher concentration (not less than about 25 g/l). No problems may therefore arise if the alcohol solution prepared is completely used every time the coating is carried out, but, when the solution is not completely used, the remaining solution must be used in a short time before it can be reused. The zirconium octylate has also a large molecular weight of the organic acid group with respect to zirconium, and therefore the yield of

zirconia is as low as about 19%.

In the method (3), the solution can attain a superior workability and give a thicker film at the first coating than other methods. In this method, however, since the acetylacetonate metallic complex is solid, its solubility to organic solvents such as alcohols and aromatic hydrocarbons is not so good that a suspension thereof can only have a concentration of about 0.05 mol/l. For this reason, the film thickness obtained by the first coating is still insufficient, and it has been necessary for obtaining a thick film to use as a solvent a highly viscous solvent such as methyl cellulose or glycol, or increase the coating times.

## SUMMARY OF THE INVENTION

An object of the present invention is to provide a method of preparing a zirconia film with a sufficient thickness by the first coating.

Another object of the present invention is to provide a method of preparing a zirconia film by using a coating solution having a superior shelf stability and achievable of a good workability.

According to the present invention, the method comprises coating a substrate with a zirconium acetylacetonate suspension formed into a sol obtained by carrying out hydrolysis of zirconium acetylacetonate by adding water in an amount of from 10 to 12 mols per mol of zirconium acetylacetonate in an organic solvent solution comprising zirconium acetylacetonate, or an organic solvent solution comprising zirconium acetylacetonate and a different type of acetylacetonate metallic complex added. This method can obtain a thick film at the first coating, and the coating solution used in the method can be stably stored for a long period of time.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

The zirconium acetylacetonate  $(\text{CH}_3\text{COCHCH}_3)_4\text{Zr}$  is a coordinate bond compound, and hence can be formed into a sol by carrying out hydrolysis by adding water, thus making its concentration higher than that in a saturated organic solvent solution. This higher concentration makes it possible to apply the compound in a large quantity than that of a saturated organic solvent solution at the first coating, to provide a thick zirconia film after heating.

The theoretical water quantity necessary for completely hydrolyzing the zirconium acetylacetonate is 4 mols per mol of zirconium acetylacetonate, but the water is added in an amount of from 10 to 12 mols. An amount less than 10 mols can not bring about complete dissolution of the zirconium acetylacetonate, resulting in a formation of a suspension, making it impossible to give a thick film at the first coating. An amount more than 12 mols may result in a white and turbid solution in several minutes after hydrolysis to produce precipitates, making it im-

possible to carry out coating.

In an instance where a different type of acetylacetonate metallic complex is added in addition to the zirconium acetylacetonate for the purpose of improving the properties of the zirconia film, it is also hydrolyzed by water and formed into a sol, and thus a thick film can also be obtained. It includes, for example, titanium acetylacetonate, aluminum acetylacetonate, potassium acetylacetonate, and diethylthallium acetylacetonate, which can be readily hydrolyzed.

Thermal decomposition after the coating of the zirconium acetylacetonate (and/or the different type of acetylacetonate metallic complex) formed into the sol, may be carried out at 200°C or more in the same manner as conventionally done. To crystallize the zirconia film, the film may be heated at from 500 to 1,200°C.

#### EXAMPLES

The present invention will be described below in greater detail by giving Examples.

##### Example 1

In a butanol suspension of 0.51 mol/l (250 g/l) of zirconium acetylacetonate, water was added in an amount of 10 mols per mol of the zirconium acetylacetonate, followed by stirring with a stirrer to make it into a sol.

Next, into the resulting zirconium acetylacetonate suspension formed into a sol and the suspension (control) having been not formed into a sol, stainless steel sheets (SUS304) of 0.4 mm thick each, subjected to ultrasonic degreasing with acetone, followed by pickling and washing with water, were respectively immersed, and drawn up at a constant rate of 0.1 mm/sec which were then put in an electric furnace heated at 400°C for 10 minutes to form zirconia films on the stainless steel sheets.

The resulting zirconia films had a film thickness of 0.25 µm in the instance where the suspension formed into a sol was used, and 0.05 µm in the instance where the control suspension was used. These films achieved a strong adhesion, and were free from generation of cracks and unevenness of film thickness.

The zirconium acetylacetonate suspension formed into a sol was also allowed to stand for a week in the air (relative humidity: 60 % at 25°C) and thereafter again used, but the same results were obtained as those before it was allowed to stand,

##### Example 2

In an isopropyl alcohol suspension of 0.25 mol/l (120 g/l) of zirconium acetylacetonate, water was added in an amount of 11 mols per mol of the zirconium acetylacetonate, followed by stirring with a stirrer to make it into a sol.

Next, using this zirconium acetylacetonate suspension formed into a sol and the suspension (control) having been not formed into a sol, zirconia films were formed on SUS304 stainless steel sheets of 0.4 mm thick each in the same procedures as Example 1, to obtain the results that the zirconia films had a film thickness of 0.13 µm in the instance

where the suspension formed into a sol was used, and 0.025 µm in the instance where the control suspension was used.

The stainless steel sheets on which these zirconia films were formed were heated at 800°C for 10 hours, and gains in weight by oxidation was measure to find that they were 0.06 mg/cm<sup>2</sup> in the instance where the film was formed using the suspension formed into a sol, and 0.11 mg/cm<sup>2</sup> in the instance where the film was formed using the control suspension.

##### Example 3

While stirring with a stirrer a butanol suspension of 0.25 mol/l of zirconium acetylacetonate, 0.05 mol/l of titanium acetylacetonate and 0.20 mol/l of aluminum acetylacetonate, water was added in an amount of 12 mols per mol of the total of these acetylacetonate metallic complexes to form the suspension into a sol.

Next, SUS304 stainless steel sheets were respectively coated with the resulting suspension formed into a sol and the suspension (control) having been not formed into a sol, following the same procedures as Example 1, followed by heating to thus form an oxide film comprising ZrO<sub>2</sub>, TiO<sub>2</sub> and AlO<sub>3</sub> uniformly dispersed. The film formed using the suspension formed into a sol had a thickness of 0.22 µm. On the other hand, the film formed using the control suspension had a thickness of 0.04 µm.

#### Claims

1. A method of preparing a zirconia film, comprising coating a substrate with a zirconium acetylacetonate suspension formed into a sol obtained by carrying out hydrolysis of zirconium acetylacetonate by adding water in an amount of from 10 to 12 mols per mol of zirconium acetylacetonate in an organic solvent solution comprising zirconium acetylacetonate, or an organic solvent solution comprising zirconium acetylacetonate and a different type of acetylacetonate metallic complex added, followed by heating at a temperature not lower than 200°C to form a zirconia film.



| DOCUMENTS CONSIDERED TO BE RELEVANT   |  |  |   |
|---|--|--|---|
| Category  | Citation of document with indication, where appropriate, of relevant passages                                      | Relevant to claim                              | CLASSIFICATION OF THE APPLICATION (Int. Cl.4) |
| A   | EP-A-0 125 507 (KANEAFUCHI)<br>* Page 6, line 26 - page 7, line 14;<br>page 9, lines 27,37; page 15, lines 31-36 * |  | C 23 C 18/12                                  |
| A   | US-A-4 129 434 (PLUMAT)  |  |   |
|   |  |  | TECHNICAL FIELDS SEARCHED (Int. Cl.4)         |
|   |  |  | C 23 C  |
| The present search report has been drawn up for all claims  |  |  |   |
| Place of search<br>THE HAGUE  |  | Date of completion of the search<br>06-09-1989 | Examiner<br>NGUYEN THE NGHIEP                 |
| <b>CATEGORY OF CITED DOCUMENTS</b>  |  |  |   |
| X : particularly relevant if taken alone<br>Y : particularly relevant if combined with another document of the same category<br>A : technological background<br>O : non-written disclosure<br>P : intermediate document   |  |  |   |
| T : theory or principle underlying the invention<br>E : earlier patent document, but published on, or after the filing date<br>D : document cited in the application<br>L : document cited for other reasons<br>.....<br>& : member of the same patent family, corresponding document |  |  |   |